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EPITAXIAL HEXAGONAL FERRITES FOR MILLIMETER WAVE
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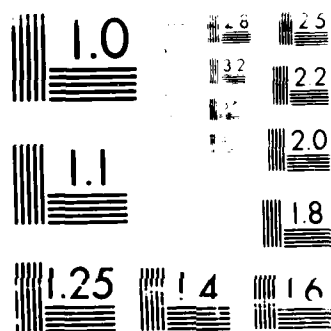
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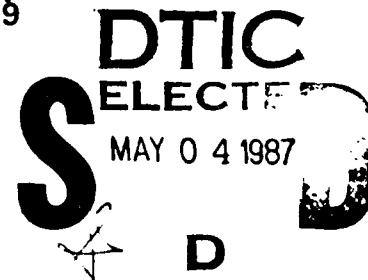
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Principal Investigator****FEBRUARY 1987**

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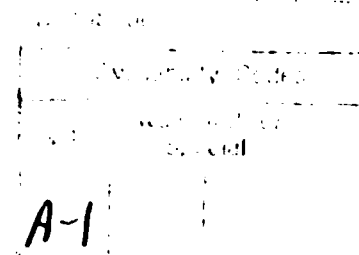
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1.0 INTRODUCTION

The objective of this research project (Contract DAAG29-83-C-0032) has been to develop single crystal hexagonal ferrite films of a quality suitable for millimeter-wave devices. The specific devices in mind were tunable filters for the 60 GHz band.

Ferrites are magnetic dielectrics.^{1,2} Among their many applications are a number of critical microwave and millimeter-wave components. These components make use of the magnetic interaction of ferrites with electromagnetic waves. Since ferrites are dielectrics, there is no skin effect to confine the interaction to a thin surface layer. In addition, certain loss mechanisms associated with electrical conduction processes can be negligibly small. Thus, ferrites are the most suitable magnetic materials at microwave and millimeter wave frequencies.

The ferrites that are commonly used in microwave components have the cubic spinel or garnet crystal structures. Examples are lithium ferrite, nickel-zinc ferrite and yttrium iron garnet (YIG). For components that operate at or close to ferromagnetic resonance (FMR), these cubic ferrites have the disadvantage that very large external magnetic bias fields are needed to achieve operation in the millimeter wave range. For example, fields of about 20 KOe (2 T), are needed for FMR frequencies near 60 GHz. Such fields are close to the limit of permanent magnet technology, and the magnet adds considerable size and mass to the component.

Hexagonal ferrites have hexagonal (or trigonal) crystal structures. Associated with the structure is a magnetic anisotropy that can be quite large. This magnetocrystalline anisotropy is in many ways equivalent to a built-in magnetic bias field that tends to align the magnetization along certain crystallographic directions. For example, in barium hexaferrite, $\text{BaFe}_{12}\text{O}_{19}$, the anisotropy field is about 18 KOe. This means that a small sphere of $\text{BaFe}_{12}\text{O}_{19}$ would have a natural resonance frequency of about 50 GHz. An external field applied in a direction to add to the internal anisotropy field would increase the resonance frequency. Thus, an applied field of 2 KOe would provide the equivalent of 20 KOe in a conventional cubic ferrite.

Hexagonal ferrites are not new materials. They have been known for over 30 years and are widely used in inexpensive permanent magnets. However, there are a num-



ber of problems to be solved before the hexagonal ferrites can be put to practical use in millimeter-wave systems. One of these problems is to prepare high-quality single crystals. Such crystals are necessary for certain devices such as narrow-band tunable filters. High-quality single crystals also are needed to study fundamental properties of hexagonal ferrites, such as the anisotropy.

There is an extensive literature on single crystal hexagonal ferrites. Probably the most significant work was done at Fort Monmouth.³ However, these bulk single crystals have certain limitations. For one thing, it is difficult to obtain high uniformity. For another, there are difficulties in fabricating devices from bulk crystals, e.g., it may be necessary to prepare spherical samples with highly polished surfaces.

The primary objective of this project has been to develop a single crystal thin-film technology for hexagonal ferrites. It should be possible to obtain high uniformity in thin films, and thin film ferrite components should be easily combined with the planar circuits and integrated circuits (MMIC, MIMIC) that are being used in millimeter-wave systems. Experience with garnet ferrites, specifically YIG, has shown that single crystal films having properties close to those of ideally perfect crystals can be grown by an LPE process.⁴ Since this process is similar to that used successfully to grow bulk crystals of hexagonal ferrites, the approach taken has been to employ an LPE process for epitaxial growth of hexagonal ferrites.

A key measure of the quality of ferrite crystals is the FMR linewidth. Linewidth is related to a number of material characteristics, some intrinsic and some extrinsic. Intrinsic characteristics are those associated with ideally perfect single crystals. For example, in YIG the linewidth at 10 GHz is less than 0.2 Oe and is associated with interactions between excitations of the spin lattice and thermal excitations of the crystal lattice (magnon-phonon scattering). Extrinsic characteristics would include the effects of impurities, defects and, in general, deviations from ideal crystal perfection.

The small intrinsic linewidth of YIG is related to the fact that the only magnetic ions are Fe and all of these are in the 3^+ valence state. This results in weak coupling between the spin and crystal lattices, and the absence of a valence exchange loss mechanism. (If some of the Fe were in a 2^+ state, an electron could transfer from a 2^+ Fe ion to a 3^+ and exchange the respective valences. This electron hopping process is driven at microwave frequencies, extracting energy from the rf field, and thus increasing



losses and linewidth.) In other ferrites, such as those containing 2^+Fe , other transition metal ions or magnetic rare earths, the intrinsic linewidth may be orders of magnitude greater than in YIG.

The small intrinsic linewidth of YIG is realized in practice because nearly perfect single crystals can be prepared. This has significant consequences for microwave devices that require single crystals. For example, narrow-band tunable filters using bulk or thin-film YIG single crystals are available. The minimum bandwidth is directly proportional to the linewidth. Tunable resonators, variable delay lines and other devices employing magnetostatic wave (MSW) propagation have been demonstrated in YIG films. The MSW propagation losses are directly proportional to the linewidth.

Several hexagonal ferrites, including the simplest, $\text{BaFe}_{12}\text{O}_{19}$, are expected to have small intrinsic linewidths. The linewidth is not expected to be as small as that of YIG, however. The high magnetocrystalline anisotropy that makes the hexagonal ferrites interesting entails a significant interaction between the Fe ions and the neighboring ions in the crystal. This implies stronger coupling between the spin and crystal lattices, and therefore higher losses. It has been estimated that the intrinsic linewidth of $\text{BaFe}_{12}\text{O}_{19}$ (with Mn doping) is 10 Oe at 60 GHz.⁵ This compares with 1 or 2 Oe for YIG at this frequency.

The smallest reported linewidth for bulk $\text{BaFe}_{12}\text{O}_{19}$ in this frequency range is 16 Oe.⁶ For epitaxial $\text{BaFe}_{12}\text{O}_{19}$, the smallest measured value reported is 62 Oe.⁶ The resonance peak was asymmetric. Assuming that the asymmetry was due to overlap of a second resonance mode, the width of the main mode was estimated by doubling the half width measured from the peak position to the nearer half power point. Doing this, a single mode value of 45 Oe was inferred.

In this project, FMR linewidth was used as the principal quantifier of crystal quality, and as a means of assessing progress toward the development of a material suitable for use in narrow-band tunable filters for frequencies in the vicinity of 60 GHz.

1.1 Epitaxial Growth

The LPE process for growth of high-quality single crystal YIG films (Fig. 1) is a form of high-temperature solution growth. As most commonly practiced, the solvent is

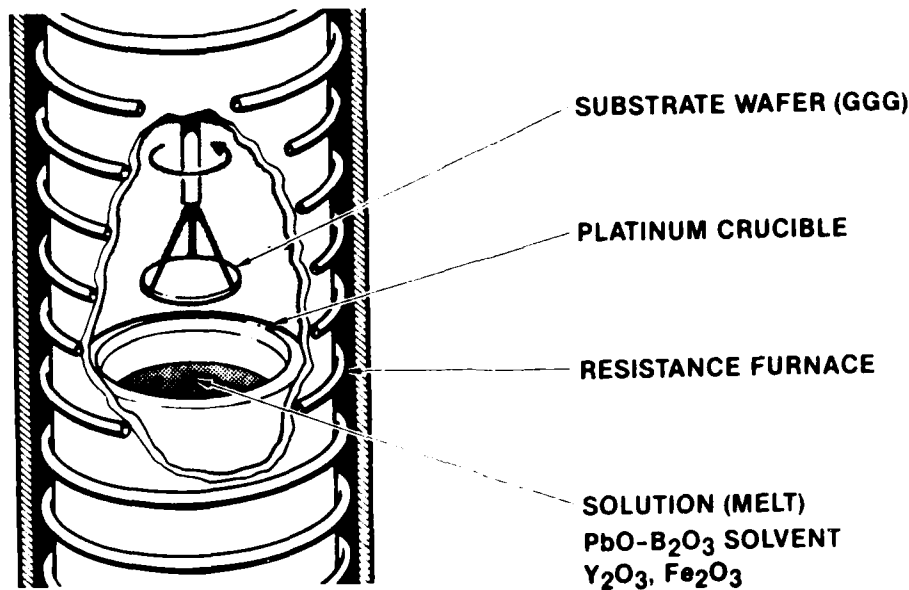


Fig. 1 Schematic of isothermal dipping method of LPE showing solution constituents for growth of YIG films.

PbO with a small addition of B₂O₃. The constituents of YIG, Y₂O₃ and Fe₂O₃ are dissolved in the solvent. A characteristic of these solutions is that they can be cooled to a temperature which is tens of degrees below the temperature at which the solution is saturated and that, in this supersaturated condition, spontaneous crystallization does not occur for a long time, at least a few hours. During this metastable interval, a suitable substrate crystal can be immersed in the solution. The substrate acts as a seed and a YIG film will deposit on its surface while the temperature is held constant. This particular LPE process is called isothermal dipping to distinguish it from other LPE techniques, such as those commonly used in compound semiconductor technology.

In this LPE method, the composition of the solution is very nearly constant during film growth. This is because the solution can be very large so that the deposition of a film extracts only a negligible fraction of the ferrite constituents. Since the temperature is also constant, the film grows at a constant rate, except for brief transient periods when the substrate is first immersed and later when the sample is pulled out of the solution. LPE YIG films are characterized by high uniformity of thickness, composition and magnetic properties.



Hexagonal ferrites can be grown by LPE using the $\text{PbO-B}_2\text{O}_3$ solvent. In the case of $\text{BaFe}_{12}\text{O}_{19}$, appropriate amounts of BaO and Fe_2O_3 are dissolved. A problem with this approach is that lead hexaferrite, $\text{PbFe}_{12}\text{O}_{19}$, also exists so the film is actually a mixed Pb,Ba hexaferrite. The magnetocrystalline anisotropy is significantly lower for $\text{PbFe}_{12}\text{O}_{19}$ than for $\text{BaFe}_{12}\text{O}_{19}$. This will result in large linewidths for the mixed hexaferrite unless the composition is quite uniform. To avoid this difficulty, one can grow $\text{BaFe}_{12}\text{O}_{19}$ from a $\text{BaO-B}_2\text{O}_3$ solvent,⁷ or one can grow $\text{PbFe}_{12}\text{O}_{19}$ from $\text{PbO-B}_2\text{O}_3$.⁸ It is also possible to use a solvent based on Bi_2O_3 . Some success has been reported using this approach;⁶ although incorporation of Bi ions, which are 3^+ , would be expected to disrupt the charge balance and introduce lossy 2^+ Fe ions which may preclude attainment of intrinsic linewidth values.

Epitaxial growth requires the availability of suitable substrate crystals. For YIG, the substrate most commonly used is gadolinium gallium garnet (GGG). GGG, like YIG, is an oxide crystal with the cubic garnet structure. These crystals can be thought of as oxygen frameworks with metal ions in sites defined by the framework. There are three distinct sites, known as c, a and d. In YIG, Y ions occupy the c-sites and Fe ions occupy the a- and d-sites. In GGG, Gd ions occupy the c- sites and Ga ions occupy the a- and d-sites. Since Ga is nonmagnetic, so is GGG (strictly speaking, GGG is paramagnetic by virtue of its Gd content). Mixed garnets can be prepared with Gd and Y substituting for one another in any proportion, and with Ga and Fe substituting for one another in any proportion. These observations point to strong physical and chemical similarities between the substrate and epitaxial film materials.

As far as YIG/GGG epitaxy is concerned, the two most significant differences between film and substrate are lattice parameter and thermal expansion. The lattice parameter (edge length of the cubic unit cell) is slightly different because of the different composition; 12.376Å for YIG and 12.383Å for GGG. This difference corresponds to a misfit (strain) of 6×10^{-4} , which is significant in generating defects or in modifying magnetic properties through stress-induced anisotropy effects. The difference in thermal expansion coefficients also can introduce significant strains over the temperature range between 900°C (a typical film growth temperature) and room temperature.

Because it is possible to prepare GGG substrates and YIG films that have no strain-relieving defects, the strains are accommodated entirely by elastic distortions. By



suitable modification of the film composition, the net strain at room temperature can be made zero. This permits the growth of thick films without fracture. Alternatively, desired anisotropy effects can be induced by deliberately creating a room-temperature strain.

With YIG/GGG epitaxy as a background, we may try to identify possible substrates for epitaxial growth of hexagonal ferrites. The obvious choice is to draw the analogy with the garnets and seek substrates that have the same crystal structure as hexagonal ferrite but which are nonmagnetic. This approach has been followed in other laboratories where substrates such as strontium hexagallate have been grown and used for LPE growth of hexagonal ferrite.

A different approach was taken in this program. A simple analysis of the crystal structures of all known hexagonal ferrites reveals that all can be described as layer structures and that all contain layers that have the cubic spinel structure.² These layers are known as S-blocks. There are two other blocks, R- and T-, and each hexagonal ferrite structure can be described by a combination of these basic building blocks in a particular stacking sequence. The stacking direction is the c-axis of the hexagonal (or trigonal) structure. Looking at the planes normal to the c-axis, the basal (0001) planes, the S-blocks are structurally identical to spinel crystals viewed on the (111) planes. The approach taken in this project was to use appropriate spinel crystals of (111) surface orientation as substrates for the epitaxial growth of hexagonal ferrites of basal (0001) orientation.

The specific spinel substrate compositions chosen for this project were zinc gallate spinel (ZnGa_2O_4 , abbreviated ZGS) and magnesium indium-gallate spinel ($\text{Mg}(\text{In,Ga})_2\text{O}_4$, abbreviated MIGS). ZGS has a lattice parameter very close to that needed to match $\text{BaFe}_{12}\text{O}_{19}$ and many other hexagonal ferrites in the (0001)/(111) epitaxy mode. In MIGS, the In:Ga ratio can be chosen to vary the lattice parameter over a range that includes the value needed to match $\text{BaFe}_{12}\text{O}_{19}$.

Another requirement imposed on the substrates is low dielectric loss. Millimeter-wave spectroscopy performed by G. Simonis at Harry Diamond Laboratories showed that a typical MIGS substrate prepared in our laboratory had extremely low loss. ZGS and strontium hexagallate are expected to have low dielectric losses also.



Both ZGS and MIGS were grown by the slow-cooling method using a $\text{PbO-B}_2\text{O}_3$ flux. The Pt crucible had a Pt rod welded to the bottom and extending out of the crystal growth furnace. The rod functioned as a heat sink and provided localized cooling at the center of the crucible bottom. This simple expedient generally resulted in growth of a small number of relatively large (1 to 3 cm) crystals on the crucible bottom. Without such localized cooling, crystals nucleated at many locations in the crucible and were much smaller.

Typical starting mixtures for substrate growth were as follows:

Chemical	Grams	Mole%
PbO	1428.39	70.07
B_2O_3	85.20	3.40
ZnO	61.45	8.27
Ga_2O_3	141.55	8.27
PbO	1454.28	70.52
B_2O_3	86.71	13.48
MgO	30.59	8.22
Ga_2O_3	106.45	6.15
In_2O_3	42.03	1.64

These amounts will fit into a one liter crucible. After the mixture melts, it will occupy less than half the crucible volume. The crystal growth procedure consisted simply of a long soak (two or three days) at a temperature of 1230 to 1260°C, followed by slow cooling at about 0.5°C/h to a temperature of about 600°C and more rapid cooling to room temperature. The crystals were released by dissolving the flux in hot, dilute acetic acid.

The spinel crystals grow with natural (111) faces. Using these as guides and x-ray diffraction for orientation refinement, (111) slices were cut, lapped and polished. The polishing process using colloidal silica was similar to that used for GGG.

Early in the project, LPE films of strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) were grown using $\text{PbO-B}_2\text{O}_3$ solvent. The solution composition was



Chemical	Grams	Mole%
PbO	87.47	32.56
B ₂ O ₃	17.58	20.98
SrCO ₃	57.86	32.56
Fe ₂ O ₃	26.72	13.90

A 50 ml Pt crucible was used. Growth temperatures were about 910°C. As explained above, Pb can freely substitute for Sr in hexagonal ferrites, so films grown from this solution actually were mixed Pb,Sr hexaferrite. We chose to try this solution because the PbO-based solvent tends to give easier nucleation on the substrate surface and more uniform films. However, linewidths at 60 GHz were several hundred oersteds. We suspected that this was due to nonuniform Pb:Sr ratio in the films, and therefore we switched to LPE growth of BaFe₁₂O₁₉ from BaO-B₂O₃ for the remainder of the project.

LPE of BaFe₁₂O₁₉ used the following starting mixture in a 250 ml Pt crucible:

Chemical	Grams	Mole%
BaCO ₃	351.10	53.53
B ₂ O ₃	70.75	30.57
Fe ₂ O ₃	84.41	15.90

Growth temperatures were in the vicinity of 920°C. Growth rates were about 0.2 μm/min.

1.2 Novel Two-Step LPE Process

Up to this point, the description of LPE growth of hexagonal ferrites has differed little from research performed prior to this project.⁷ The hexagonal ferrite films do not deposit uniformly on the substrates. In fact, ferrite may not deposit at all unless the temperature is far below the saturation condition; that is, the supersaturation is high, actually high enough for spontaneous nucleation of ferrite crystals on the surface of the solution. When ferrite does deposit, it takes the form of small hexagonal islands that eventually merge as growth proceeds (similar results have been reported for other LPE solvents and for other substrates⁶). The growth may be difficult to control because the



high supersaturation needed to initiate growth may be too high for good quality sustained growth.

It has been recognized that LPE growth of hexagonal ferrite onto hexagonal ferrite substrates can yield good quality films. This was demonstrated in early experiments,⁹ but could have been anticipated because of the similarity between LPE and the top-seeded solution growth method that had been successfully applied to these materials.³ Thus, the problem of improving the quality of hexagonal ferrite films on nonmagnetic substrates amounts to overcoming the nucleation difficulty. Once a good quality thin film of hexagonal ferrite has been deposited, subsequent film growth should be straightforward.

Our initial idea for overcoming the nucleation problem was to use sputter deposition. Two university laboratories in Japan had reported sputter deposited $\text{BaFe}_{12}\text{O}_{19}$ films that, although polycrystalline, exhibited a high degree of preferred orientation with the (0001) basal plane parallel to the substrate.¹⁰ The substrates were silica glass or other materials that were not expected to be suitable for epitaxy.

It occurred to us that if a suitable substrate were used, such as (111) MIGS, it might be possible to obtain an epitaxial film by sputter deposition. The film would probably be thin, perhaps only a few tenths of a micrometer, because sputter deposition rates are low. However, even such thin films could solve the nucleation problem.

Our initial experiments on sputter deposition of $\text{BaFe}_{12}\text{O}_{19}$ resulted in films that were tentatively identified by x-ray diffraction as having a spinel structure. It then occurred to us that a spinel ferrite film might be equally effective in overcoming the nucleation problem. Our reasoning was as follows.

ZGS, MIGS and even strontium hexagallate have been chosen as substrates because they have crystal structures that closely match the hexagonal ferrites both in atomic arrangement and in interatomic dimensions. (In addition, these substrates have physical and chemical properties that permit them to withstand the LPE environment.) The observation that hexagonal ferrite does not deposit in uniform layers on these substrates, but deposits as islands, indicates that the substrates still are not sufficiently well matched to the film. The substrates still appear too "foreign". If we deposit a spinel ferrite layer on the substrate, the surface of the spinel ferrite film may be better matched to the hexagonal ferrite and may appear less foreign (perhaps the spinel ferrite



film provides a better chemical match whereas the substrate only provides a physical match).

We chose to call this spinel ferrite film, that is grown for the purposes of obtaining a better quality hexagonal ferrite film, a spinel intermediary layer. In most of our experiments, we used lithium ferrite (LiFe_5O_8) grown by LPE from a $\text{PbO-B}_2\text{O}_3$ solvent as the spinel intermediary layer. LiFe_5O_8 has low magnetic and dielectric losses, similar to YIG, and has a lattice parameter close to that of the ZGS and MIGS substrates. Since LiFe_5O_8 has relatively low anisotropy, any resonance devices using the hexagonal ferrite film would operate far off the LiFe_5O_8 resonance. Thus, the thin LiFe_5O_8 layer should not have any significant effect on the operating characteristics of the devices.

A typical LPE solution for LiFe_5O_8 growth is

Chemical	Grams	Mole%
PbO	909.99	81.04
B_2O_3	9.80	2.80
Li_2CO_3	4.00	1.08
Fe_2O_3	121.25	15.09

These quantities are suitable for a 250 ml crucible. The growth rate at 855°C is about $0.2 \mu\text{m}/\text{min}$.

In some experiments, we used Al-substituted zinc ferrite ($\text{Zn}(\text{Al},\text{Fe})_2\text{O}_4$) as the spinel intermediary layer. The Al substitution was chosen to provide a suitable value of lattice parameter. LPE with $\text{PbO-B}_2\text{O}_3$ solvent was used. Also, we performed some experiments using Zn-substituted or Zn/Al-substituted LiFe_5O_8 intermediary layers. In all these cases, we were interested in seeing whether the presence of Zn would influence hexagonal ferrite growth. Research performed on an earlier contract with AFOSR showed that the presence of ZnO in the LPE solution facilitated nucleation of $\text{BaFe}_{12}\text{O}_{19}$.⁷

The LPE growth of these spinel ferrites had certain characteristics. There is an interaction with the substrate that seems to produce a diffused or graded layer. This can result in a coloring of the substrate that may be mistaken for a thin film. The (111) plane is a facet surface (natural face) for spinels and there is a tendency for the film to



form hillocks or growth terraces. The film growth is strongly influenced by the presence of substrate defects. These characteristics were known from previous work on LPE of spinel ferrites done in our laboratory and elsewhere.

In general, we found that the use of spinel intermediary layers provided several benefits. First, the $\text{BaFe}_{12}\text{O}_{19}$ films could be grown on top of these layers at temperatures closer to the saturation temperature; that is, at lower supersaturation. Second, the films were much more uniform than films grown directly on the ZGS or MIGS substrates. The pronounced hexagonal island morphology usually seen on ZGS or MIGS was absent; however, rounded hillocks were generally observed. Third, the hexagonal ferrite films were securely attached to the intermediary layers and substrates. This is in contrast to direct growth on ZGS and MIGS for which fragments of film easily became detached. Fourth, some of the hexagonal ferrite films grown on spinel intermediary layers exhibited significantly smaller linewidths at 60 GHz than any of our earlier films; similar to the best reported value in the literature.

1.3 Ferromagnetic Resonance

FMR measurements were made at frequencies near 60 GHz using both transmission and reflection mode spectrometers. The transmission spectrometer consisted of an Impatt signal source, a frequency meter, and a flat band detector connected together sequentially by straight rectangular metal waveguides. The hexagonal ferrite sample was placed near the inner wall of one transmission waveguide segment. This segment was located between the poles of a laboratory electromagnet. For the reflection mode, the transmission waveguide was terminated with a short and the reflected energy was brought out to the detector by a directional coupler. In this configuration, the hexagonal ferrite sample was placed near the shorted end and this was positioned between the poles of the magnet.

In operation, the magnet was used to provide the dc bias field that set the resonance frequency. Resonance was observed as a dip in transmitted or reflected power when either the dc magnetic field or the frequency of the rf field was swept through the resonance condition. The dip corresponds to power absorbed in the ferrite sample at resonance. In the configurations described, the apparatus functions as a tunable bandstop filter.



During the early part of the project, measurements were made using swept frequency (51 to 61 GHz) and fixed dc magnetic field. Linewidths of about 50 or 60 Oe (at half power) were measured on some of the early $\text{BaFe}_{12}\text{O}_{19}$ samples. Similar values were obtained on samples sent to Fort Monmouth (A. Tauber, L. Silber and W. Wilbur, ETDL) where measurements were made using fixed frequency and swept dc field.

Subsequently, films having lower linewidths were prepared. Typically, these samples exhibited resonance peaks that tuned from 54 to 60 GHz as the dc magnetic field was increased from 7.2 to 9.2 KOe. These values of dc field are within a few hundred oersted of the values expected for $\text{BaFe}_{12}\text{O}_{19}$. Linewidths were about 30 Oe, with some values even smaller. However, when measured by the fixed frequency method at Fort Monmouth and at Naval Research Laboratory (P. Lubitz), the linewidths were found to be little different from the earlier samples, 50 to 60 Oe.

We have not been able to account for the difference between the fixed frequency and swept frequency results. They should be equivalent. We modified our setup so that fixed frequency measurements could be made. In this configuration, we used Gunn oscillator as well as *Impatt* diode signal sources. With this apparatus, we obtained linewidth values similar to those measured at Fort Monmouth. Also, we observed that all samples showed more than one resonance mode, sometimes as a peak asymmetry, sometimes as additional resolved peaks (Fig. 2).

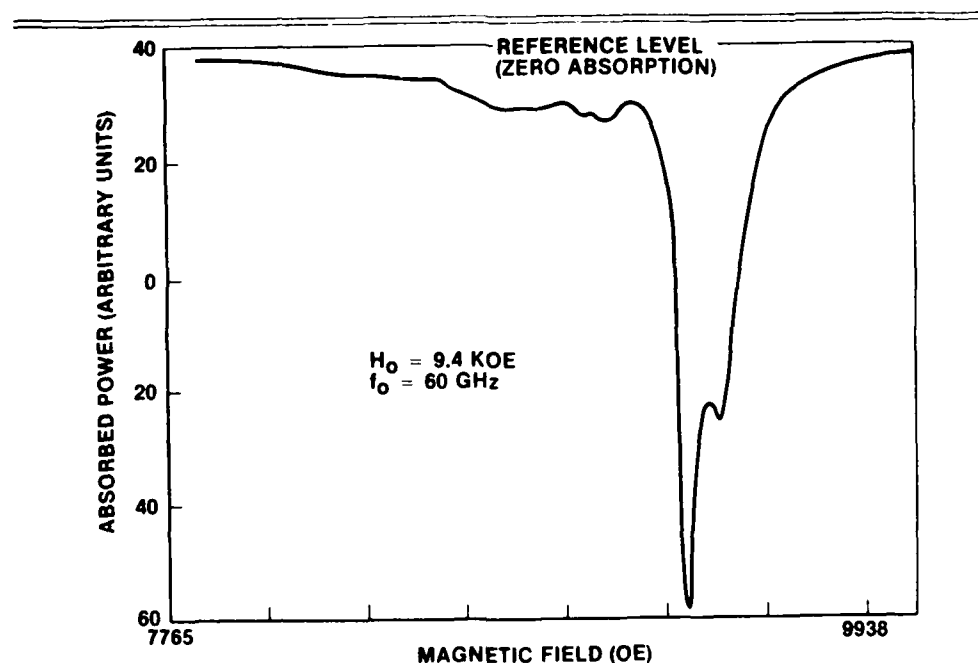


Fig. 2 60 GHz FMR absorption spectrum for a $\text{BaFe}_{12}\text{O}_{19}$ film grown by the two-step LPE method on a MGS substrate. The measurement was made using the reflection mode spectrometer with the dc magnetic bias field applied perpendicular to the plane of the film. The magnetic bias field strength at the resonance peak is 9.4 KOe. The linewidth of the principal resonance mode is 54 Oe.



2.0 PRESENT STATUS

The research on LPE growth of hexagonal ferrites using spinel intermediary layers is far from complete. While some improvements in film quality have been obtained, linewidths are not yet as low as expected. In addition, the films are not generally smooth and uniform and film quality is quite variable.

The following discussion deals with several observations and tentative conclusions.

When LiFe_5O_8 is used as the spinel intermediary layer, there is an optimum thickness, approximately $1\text{ }\mu\text{m}$. If the film is too thick, it fractures. This may be due to the relatively large thermal expansion coefficient compared to the substrate. If the film is too thin, it tends to dissolve during the initial stages of the hexagonal ferrite epitaxy step.

Dissolution of the LiFe_5O_8 is not surprising since the hexagonal ferrite LPE solution, although supersaturated with respect to hexagonal ferrite, is unsaturated with respect to the LiFe_5O_8 . It is possible that this dissolution plays a key role. The dissolved spinel layer constituents may alter the composition of the LPE solution immediately adjacent to the substrate and then be redeposited as part of a hexagonal ferrite of modified composition. If the spinel intermediary layer is too thin, it may dissolve without any subsequent deposition of hexagonal ferrite.

The Al-substituted zinc ferrite seemed to be more reactive. It dissolved more readily during hexagonal ferrite LPE. Hexagonal ferrite could be deposited at higher temperatures (lower supersaturation) than for LiFe_5O_8 intermediary layers. This shows that the zinc ferrite is more effective at facilitating hexagonal ferrite nucleation. However, there was no significant difference between the two intermediary layer compositions in terms of hexagonal ferrite quality.

All of the hexagonal ferrite films contained many hillocks. Unlike the hexagonal islands or scales seen in films grown directly on MIGS or ZGS substrates, these hillocks were rounded. The hillock surfaces often were irregular. Other features included ridges, fractures, banding and regions with rough, micrometer size textures. The samples that gave the smallest linewidths were those that contained large hillocks, nearly 1 mm in diameter, so that a small FMR sample consisted mainly of a single hillock. The presence of additional resonance modes may be due to the presence of more than one hillock.



The morphological features on the hexagonal ferrite film surfaces seemed to correspond to similar features in the spinel intermediary layers. In the spinel layers, the hillocks often contained growth spirals. Such features usually result from the presence of dislocations that act as preferred nucleation sites for growth on facet surfaces. Different areas of the same sample frequently exhibited markedly different morphologies, sometimes with sharp boundaries between the different areas. For example, a relatively smooth area would be adjacent to an area covered with parallel ridges.

The foregoing observations about the morphology of the hexagonal ferrite films and the spinel intermediary layers strongly suggest that the origin of most defects is in the substrate. We evaluated several different substrate surface treatments, but these had no effect on the results. Thus, the problem seems to lie in the bulk of the substrates rather than in surface damage.

X-ray topography (Fig. 3) was used to examine the substrates. In general, the substrate crystal quality is high compared to typical oxide single crystals. The dominant feature revealed by topography is variation in lattice parameter. This variation may be

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Fig. 3 FeK α x ray double-crystal (620) reflection topograph of (111) MGS substrate crystal showing growth band pattern and localized defects. Field of view is 1.2 mm x 1.6 mm.



attributed to fluctuations in composition, e.g., fluctuations in the incorporation of Pb as an impurity from the PbO-based flux or fluctuations in the In:Ga ratio. The magnitude of these variations is small, at most about 0.001\AA , or about 1×10^{-4} expressed as a strain. The variation takes several forms: a banding pattern that is common in flux-grown crystals generally and is also seen in crystals pulled from the melt; a growth sector pattern that corresponds to intersections of the various facets, also common in flux-grown crystals; a long-range variation that may correspond to a dependence of crystal composition on growth temperature and flux composition, and would be associated with the use of a large-temperature interval for the growth.

The topographs also showed images of localized defects. Most of these appeared to be dislocations. The dislocations are not randomly distributed, but a fair estimate of their density is something on the order of $10^2/\text{cm}^2$. This corresponds to the observed density of hillocks; however, we have not established a one-to-one correspondence. Band and ridge patterns in the films may correspond to band patterns in the substrates.

Fracture in the films seems to be related to film thickness. For example, taller hillocks may contain fractures, while lower hillocks and surrounding flat areas do not. This suggests that the fracture is associated with stress in the film. The relief of film stress by the generation of fracture or other defects is characterized by a critical film thickness for a given stress value. For films that exceed the critical thickness it is energetically favorable to generate defects, such as cracks, that reduce the elastic strain energy.

The substrates have been chosen to have lattice parameters that closely match the films. Therefore, we expect the film stress to be small. However, this is true only near room temperature. In general, ferrites have larger thermal expansion coefficients than the substrates. This means that at the growth temperature the films are under compressive misfit stress. In YIG, this is not a problem. No defects are generated, even when the compressive stress is quite large, and the stress simply gives rise to elastic distortions. Perhaps the spinel and hexagonal ferrites are more susceptible to defect generation.

Obviously, additional research is needed to obtain further improvements in film quality.



3.0 FUTURE DIRECTIONS

The basic approach involving a two-step film growth process with the hexagonal ferrite film grown by LPE onto an intermediary layer appears to be very promising. The major problem seems to be substrate crystal quality and future work should address this problem. In addition, there may be better choices for the intermediary layer composition and deposition method. LPE remains highly attractive as a technique for preparing single crystal hexagonal ferrite films of a quality and thickness (tens of micrometers) suitable for millimeter-wave devices. The best LPE process will need to be determined once the substrate and intermediary layers have been improved. In addition, specific hexagonal ferrite types and compositions must be optimized for particular device configurations and operating frequencies. These remaining tasks will now be discussed briefly.

Two major factors in choosing gallate spinels as substrates are: first, magnesium gallate spinel (MGS, or MIGS with In content of zero) can be grown directly from the melt by a process that is quite similar to that used commercially to grow GGG; second, there has been a demonstration of (111) epitaxial growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ on (111) MGS. The first factor indicates that MGS is a commercially practical substrate. The second factor suggests that monolithic integration of epitaxial ferrites and semiconductors is possible. This is significant for compatibility with MMIC and MIMIC structures and for future integration with photonic systems; for example, future systems may use integrated optical computers for signal processing in millimeter-wave receivers.

MGS has a lattice parameter that is slightly too small for matching $\text{BaFe}_{12}\text{O}_{19}$. However, as in the case of YIG, matching can be achieved by altering the ferrite composition in the LPE process. For example, a partial substitution of Al for Fe will reduce the ferrite lattice parameter and provide the necessary matching. In addition, Al substitution is expected to reduce thermal expansion mismatch.

It is well established that Al substitution will lower the magnetization; however, this has the effect of increasing the anisotropy field. Therefore, Al-substituted $\text{BaFe}_{12}\text{O}_{19}$ will require smaller external magnetic fields, a factor that becomes particularly significant for operation at 94 GHz and higher frequencies. The effect of Al substitution on anisotropy field means that the substitution must be extremely uniform if small



linewidths are to be maintained. This will be possible only if the film growth is uniform, another reason for eliminating the hillock structure.

There are several approaches toward improved substrate crystal quality. One approach is to use the Czochralski method of growth from the melt. This method is used to grow dislocation-free GGG. However, developing the necessary procedures is a lengthy and expensive process. (It took several years to develop the GGG process; however, MGS growth should benefit from that experience.)

Flux growth is a simple, low-cost method that tends to produce good quality crystals. The present dislocation density of about $10^2/\text{cm}^2$ is low compared to, say, Czochralski-grown sapphire. Certain modifications may reduce the dislocation density. One would be to develop procedures for obtaining larger crystals. If the total number of dislocations remains the same or if the dislocations tend to concentrate in certain regions such as the boundaries of the growth sectors, then the dislocation density decreases as the size increases. The use of seeded growth rather than free nucleation (the present method) may help produce larger crystals with lower dislocation density. All one needs at this stage is to obtain some areas that are dislocation-free to demonstrate small linewidths and to justify more extensive development of substrate technology.

Although gallate spinels, particularly MGS, seem to be good choices for substrates, the ultimate test is whether high-quality films are obtained. Therefore, other substrates, including hexagallates, should be considered. The two step film growth process using an intermediary layer should be useful with these other substrates.

The specific choice of intermediary layer composition may not be critical; although the results with Al-substituted zinc ferrite show that there are significant effects. The most important requirement is good crystal quality in this layer. Other compositions or other deposition techniques may prove advantageous. For example, although LiFe_5O_8 is attractive because its lattice parameter is about right, its large thermal expansion coefficient may be troublesome. Other spinel ferrites, particularly with Al substitution, may be found more suitable. Also, LPE spinel ferrites films of (111) orientation tend to contain growth terraces. Other deposition techniques, e.g., chemical vapor deposition or sputter deposition, could be better. However, LPE, which is simple and well established, appears to yield the best quality spinel ferrites. Perhaps the problem of terraces will not be significant for the relatively thin layers that are needed.



For growth of the hexagonal ferrite film, LPE is probably the best technique. As explained previously, highly uniform films tens of micrometers thick should be obtainable if the nonuniformities associated with defects (hillocks, ridges, etc.) can be avoided. The LPE method is very similar to the technique used to grow bulk crystals in which linewidths as low as 16 Oe have been reported. The bulk crystals have been grown using $\text{BaO-B}_2\text{O}_3$ solvents. Although we have been using this solvent system for LPE, it is possible that some other solvent system will give better results.

The only reason to doubt that LPE films can be at least as good as bulk crystals is the potential problem of antiphase defects. These defects could arise if the film starts growing with different layers on different areas of the substrate. For example, in one area the film may first deposit an S-block while in another area it may first deposit an R-block. Then the overall film would contain a kind of disorder that might increase linewidth. Such antiphase defects are only speculative at this point. If such defects occur and are troublesome, it may be possible to control them by choice of substrate or intermediary layer. This is a potential problem to be aware of once the more immediate problems of improving crystal quality are solved.

Another task for future research is the growth of hexagonal ferrite types other than the simple $\text{BaFe}_{12}\text{O}_{19}$. $\text{SrFe}_{12}\text{O}_{19}$ is of interest because of its somewhat higher anisotropy; however, $\text{SrO-B}_2\text{O}_3$ is not an appropriate solvent for LPE, so some other solvent system would be necessary. The more complex hexagonal ferrite types (referred to as W-type, Z-type, etc.) are more difficult to grow. It is not clear at this time whether they would be more suitable than the simpler hexagonal ferrites for millimeter-wave devices. If these other types are desired, the LPE method in which growth is carried out at constant temperature and constant solution composition, should be more controllable than the bulk crystal growth methods.

In summary, there seem to be clear directions for near-term research on growing single crystal hexagonal films of superior quality.



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4.0 PERSONNEL

The principal technical contributors to this project were H. L. Glass, L. R. Adkins and F. S. Stearns of the Rockwell International Science Center.



5.0 PUBLICATIONS

An invited paper, "Thin-Film Ferrite Materials for Microwave and Millimeter-Wave Integrated Circuits," by H.L. Glass, was presented at the 1986 Conference on Magnetism and Magnetic Materials. The presentation included a description of some of the research performed on this project. An abstract of the talk will be published in the Journal of Applied Physics Supplement that constitutes the conference proceedings.

A paper describing the two-step LPE method for growth of hexagonal ferrite films on gallate spinel substrates was planned for the 1987 INTERMAG Conference. Unfortunately, we were not able to attend that conference. The paper will be submitted to a future magnetism conference.

The two-step LPE process is described in U.S. Patent Number 4,624,901, "Intermediary Layers for Epitaxial Hexagonal Ferrite Films," issued November 25, 1986. The invention was made with Government support under a previous contract with the Air Force. However, the reduction to practice, which formed the basis of the examples cited in the patent, was made under the Army contract that is the subject of this report.



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